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Mixed alkali effect in physical and optical properties of Li_2O–Na_2O–WO_3–B_2O_3 glasses

A. Edukondalu [a], M. Purnima [a], Ch. Srinivasy [a], T. Sripathi [b], A.M. Awasthi [b], Syed Rahman [a,*], K. Siva Kumar [a]

[a] Department of Physics, Osmania University, Hyderabad 500 007, India
[b] Consortium for Scientific Research, Khandwa road, Indore 452 017, India

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ABSTRACT

Glasses with composition xLi_2O-$(30-x)Na_2O$–$10WO_3$–$60B_2O_3$ (where x = 0, 5, 10, 15, 20, 25 and 30 mol%) have been prepared using the melt quenching technique. In the present work, the mixed alkali effect (MAE) has been investigated in the above glass system through density and modulated DSC studies. The density and glass transition temperature of the present gasses varies non-linearly, the exhibiting the mixed alkali effect. From the optical absorption studies, the values of direct optical band gap, indirect optical band gap energy (E_o) and Urbach energy(ΔE) have been evaluated. The values of E_o and ΔE vary non-linearly with composition parameter, showing the mixed alkali effect. The electronic polarizability of oxide ions, optical basicity and the Yamashita–Kurosawa's interaction parameter have been examined to check the correlation among them and bond character. Based on good correlation among electronic polarizability of oxide ions, optical basicity and the Yamashita–Kurosawa's interaction parameter, the present Li_2O–Na_2O–WO_3–B_2O_3 glasses were classified as normal ionic (basic) oxides.

1. Introduction

A glass exhibits non-linear variation in its properties which include density, viscosity, glass transition temperature and conductivity when one alkali component in a multi component glass is systematically replaced by another alkali species. This phenomenon is referred to as the mixed alkali effect (MAE) and is useful in manufacturing low loss electrical glass [1]. Models for MAE have been proposed in the literature and compiled in several reviews [1–3]. Recently, Belostotsky [4] reported a new defect model for the mixed alkali effect. The essential physical concept involved is that simultaneous migration of two unlike alkali ions in mixed ionic glass is accompanied by an expansion or contraction of the guest-occupied sites with distortion of the surrounding glass matrix [5]. Far infrared spectroscopy has been employed to probe the effect of alkali mixing on the interactions between alkali ions and local sites in mixed alkali glasses [6,7]. Maass et al. developed the dynamic structure model to explain the mixed alkali effect [8]. To study the mixed alkali phenomenon, borate glasses proved to be promising hosts to investigate the influence of chemical environment, structural diversity of ligand groups and spectroscopic properties of the materials [9].

Tungsten ion containing glasses have gained much importance due to their non-linear optical absorption and electrical properties for technological applications [10–12]. Tungsten ions are predicted to have stronge influence on physical properties of compounds. In oxide glasses, tungsten ions are generally assumed to attain multiple oxidation states, such as hexavalent W^{6+}, pentavalent W^{5+} and also tetravalent W^{4+}, regardless of the oxidation state of the tungsten ion in the starting glass batch [13]. W^{6+} ions participate in the glass network with different structural units, like WO_4 (T_d) and WO_6 (O_h) structural units and W^{5+} ions participate in the form of $W^{5+}O_3^-$, and occupy octahedral positions [14]. Thus the concentration of different structural groups of tungsten ions with different oxidation states present in the glass matrix at a given temperature depends on the quantitative properties of modifiers, glass formers, size of ions in the glass structure, mobility of the modifier cation etc. W^{5+} ions are well known paramagnetic ions. The presence of tungsten in borate glasses, further, makes these glasses suitable for optoelectronic devices since they exhibit photochromism, electrochromism and thermochromism properties, which are known for provoking a color change due to the action of electromagnetic radiation, electric field, and heat respectively [15,16]. These glasses have several advantages over crystalline counterparts, such as easy formability over wide ranges of composition, isotropicity, absence of grain boundaries and ease of fabrication in complex shapes, which make them particularly attractive in practical applications [17,18].

The ability of boron to exist in both three-and four-coordinated environments and high strength of the covalent B-O bonds imparts

* Corresponding author.
E-mail address: syedrahman848@yahoo.co.in (S. Rahman).

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borates to form stable glasses. The B_2O_3 glasses are well known due to their large photo-induced second-order non-linear optical effects that have strong bearing on luminescent efficiencies of these glasses [19]. Alkali borate glasses are well known due to their high transparency, low melting point, high thermal stability, and good rare earth ion solubility [20,21]. However, interest in these glasses is limited as laser hosts due to their high phonon energy. Nevertheless, the addition of some transition metal oxide like WO_3 to Li_2O-B_2O_3 glass makes them more moisture resistant, and the phonon losses can also be minimized to a large extent. Tungsten-containing glasses have been studied for the favorable properties of tungsten ions, such as high electro-negativity, polarizability, large ion radius, and changeable valance [22,23]. Glasses with high WO_3 contents and short reaction time show blue coloration. The blue transition depends on the mixture of W^{5+} and W^{6+} [24–27]. Arghavani et al. reported the blue coloration of $(Li_2B_4O_7)_{1-x}(WO_3)_x$ glasses for high concentration of WO_3 in terms of inter-valence electron transfer [28]. For a value of $x \leq 0.33$, glasses are transparent [24], which can be used for modeling typical glass applications such as sensors for the investigation of structural aspects of the amorphous materials [29,13]. Tawarayama et al. reported that during heat treatment, the $30Na_2O$–$10BaO$–$30P_2O_5$–$20Nb_2O_5$–$10WO_3$ glass is permeable to hydrogen, and as monoatomic hydrogen passes through the glass, it is reducing tungsten ions from W^{6+} to W^{5+} [30,31]. They proposed that the fast coloration requires fast diffusion of electrons and protons introduced into the glass. Sugata et al. have shown that hydrogen diffusion in alkali tungsten phosphate glasses depends on the alkali type [32].

To reveal the role of WO_3 in the glassy borate network, Gaffar et al. studied the FTIR and ultrasonic properties on Li_2O–WO_3–B_2O_3 glasses [33,34]. El Batal [35] performed optical UV-visible, infrared, EPR, and Raman spectral studies of some lithium borate glasses containing varying WO_3 contents before and after gamma ray irradiation. Ali Abou Shama carried out structural studies in lithium tungsten borate glasses, and also correlated with the other measured physical properties such as electrical conductivity, and activation energy [36]. Sheoran et al. measured the variation of density, molar volume, and optical basicity with glass composition and complex impedance of alkali tungsten borate glasses [37]. Deal et al. reported Raman and luminescence studies on Na_2O–B_2O_3–WO_3 glasses [38]. They reported that, at low concentrations of WO_3 a tetrahedral structural unit WO_4 was formed and increased as the WO_3 concentration increased. At high concentrations, both WO_4 and a new octahedral species WO_6 were formed.

Many investigations have been reported on ternary alkali tungstate in phosphate, borate, tellurite, bismuthate, and niobate glasses [39–43]. More recently, Salem *et al.* presented physical, structural, optical, and dielectric properties of $15Li_2O$–$(65-x)Bi_2O_3$–$20GeO_2$–xWO_3 glasses (where $x = 2$, 5, 10 mol%) [44]. To the best of our knowledge, there are no reports on mixed alkali borate tungsten glasses. A recent investigation of the electrical, glass transition temperature, and density properties in Li_2O–Na_2O–$WO_3(MoO_3)$–P_2O_5 system showed the mixed alkali effect [5,45].

The aim of the present work is to investigate the mixed alkali effect in xLi_2O–$(30-x)Na_2O$–$10WO_3$–$60B_2O_3$ ($0 \leq x \leq 30$ mol%) glasses by measuring the physical properties which include density, refractive index, and glass transition temperature as a function of compositional parameter R_{Li}, which is defined as $R_{Li} = Li_2O(mol\%)/(Li_2O + Na_2O)(mol\%)$. R_{Li} takes the values 0, 0.166, 0.33, 0.5, 0.66, 0.83 and 1. Further, optical absorption studies have also been performed on glass samples.

2. Experimental

A batch of approximately 15 g of chemicals in powder form was weighed using a digital balance with an accuracy of ±0.01 mg. The relative weights of the components were calculated according to the molar formula xLi_2O–$(30-x)Na_2O$–$10WO_3$–$60B_2O_3$, where *x* ranged between 0 and 30 mol%. The glass composition, compositional parameter and glass preparation temperature are listed in Table 1. Appropriate amounts of reagent grade Li_2CO_3, Na_2CO_3, H_3BO_3, and WO_3 were well-mixed and melted in porcelain crucibles in the temperature range of 1100–1150 °C, depending on the glass composition, in an electrical muffle furnace for about 60 minutes. The porcelain crucibles containing glass melt was swirled frequently to insure the homogeneity. The clear liquid (free of bubbles) was quickly cast in a stainless steel mould kept at 200 °C and pressed with another steel disc maintained at same temperature. Later, the samples were annealed 100 °C below their respective glass transition temperature for about 24 hours and slowly cooled to laboratory temperature.

The amorphous nature of the glass samples was confirmed by X-ray diffraction study. An advance powder XRD (PANalytical X-pert PRO model with Cu–K Alpha radiation of wavelength 1.54048 Å) was used. The room temperature density (ρ) of the samples was determined by the Archimedes principle. Xylene was used as an immersion liquid. The densities were calculated by using the formula

$$\rho = a * 0.86/(a-b) \quad (1)$$

where **a** is the weight of the sample measured in air, **b** is the weight of the sample measured in xylene (density of xylene at room temperature is 0.86 g/cc). The uncertainty in density measurement is ± 0.001 g/cc. The molar volume of the glass samples was calculated using the formula

$$V_m = M/\rho \quad (2)$$

where M is the average molecular weight of the glass and ρ is its density. From the density data, oxygen packing density was calculated by using the formula

$$\text{Oxygen packing density} = (\rho/M) \times \text{number of oxygen atoms per formula unit.} \quad (3)$$

The lithium ion concentration (N), the average lithium inter ionic separation (R) and the polaron radii (r_p) were calculated by the following relations.

$$N = 6.023 * 10^{23} * \text{mol\% of cation} * \text{valancy of cation}/V_m \quad (4)$$

$$R = (1/N)^{1/3} \text{and } r_p = (1/2)(\Pi/6\,N)^{1/3} \quad (5)$$

The refractive indices of the prepared glasses were measured using Abbe's refractometer. The thermal behavior of the glass samples was investigated using a modulated differential scanning calorimeter (TA Instruments model 2910). Glass samples weighing about 15 mg

Table 1
Glass composition, compositional parameter R_{Li} and preparation temperature of the present glass system.

Glass composition	Compositional parameter R_{Li}	Preparation temperature (°C)
$30Na_2O$–$10WO_3$–$60B_2O_3$	0	1100
$5Li_2O$–$25Na_2O$–$10WO_3$–$60B_2O_3$	0.166	1112
$10Li_2O$–$20Na_2O$–$10WO_3$–$60B_2O_3$	0.33	1121
$15Li_2O$–$15Na_2O$–$10WO_3$–$60B_2O_3$	0.5	1125
$20Li_2O$–$10Na_2O$–$10WO_3$–$60B_2O_3$	0.66	1130
$25Li_2O$–$5Na_2O$–$10WO_3$–$60B_2O_3$	0.83	1140
$30Li_2O$–$10WO_3$–$60B_2O_3$	1	1150